

Bonding of Silicon Carbide Based Ceramics using Particulate Reinforced Ag-Cu-Ti Alloys

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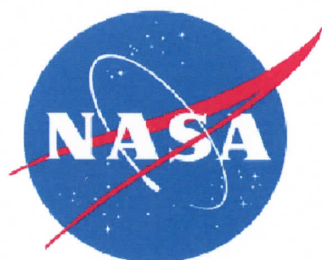
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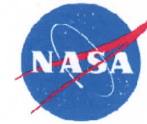
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**36th International Conference and Exposition on Advanced Ceramics and Composites,
Daytona Beach, Florida, January 22 – 27, 2012.**



Outline

- **Background and Introduction**
 - Potential Applications
- **Experimental Details**
 - SiC Brazing using Ticusil
 - SiC Brazing using TiCusil + SiC particles
- **Characterization**
 - Optical Microscopy
 - Scanning Electron Microscopy (SEM)
 - Energy Dispersion Spectrometry (EDS)
 - Microhardness Measurements
- **Summary and Conclusions**



Need for Joining and Assembly Technologies

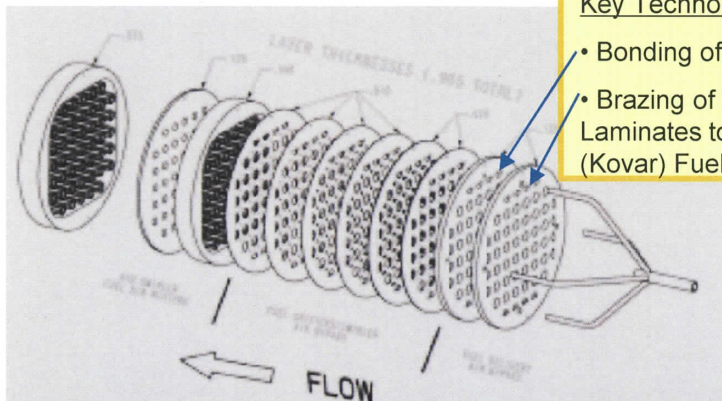
- **Joining is an enabling technology for utilization of advanced ceramics and composites in high temperature applications.**
 - **Aerospace Systems**
 - *Aerospace and Space Propulsion Components (Combustor Liners, Exhaust Nozzles, Nozzle Ramps, Turbopump Blisks)*
 - **Non-Aerospace Systems**
 - *Nuclear Industries, Land Based Power Generation, Process Industries, Heat Exchangers, Recuperators, Microelectronic Industries (Diffusion Furnace, Boats)*
- **The development of ceramic joining and assembly capability will allow the application of advanced ceramics and composites technology in a timely manner.**



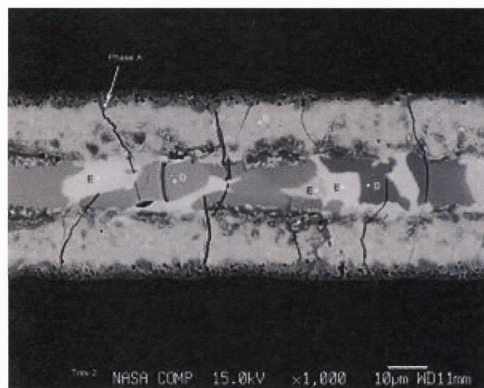
Critical Need for Joining and Integration Technologies in Fabrication of MEMS Lean Direct Injector

Key Technologies:

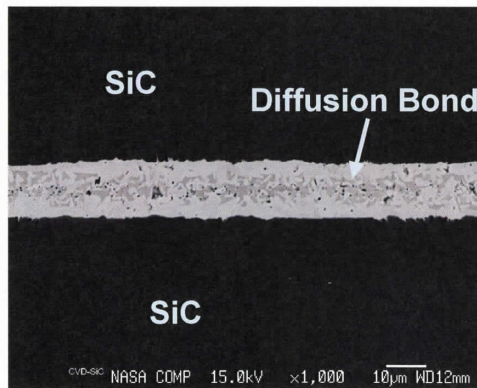
- Bonding of SiC to SiC
- Brazing of SiC Laminates to Metallic (Kovar) Fuel Tubes



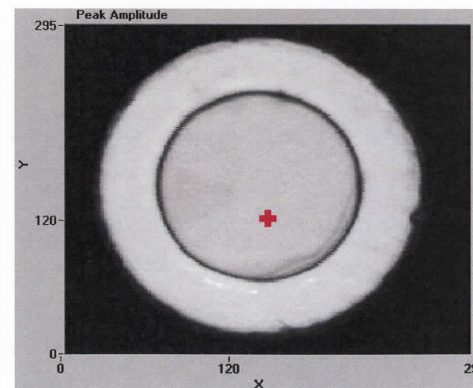
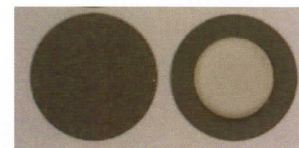
Previous joining approach using silicate glass resulting in plugged fuel holes and leaks in the SiC injector.



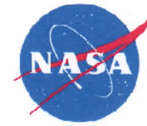
Un-optimized diffusion bond using a 38 micron thick alloyed Ti foil for an interlayer. Microcracks and non-uniformity are seen.



Optimized diffusion bond using a 10 micron thick PVD coating for an interlayer. A uniform bond with no microcracking is observed.



Above: Unbonded 1" SiC discs with a 0.65" diameter Ti coating on one of the discs.
Below: Ultrasonic C-scan image of bonded discs.



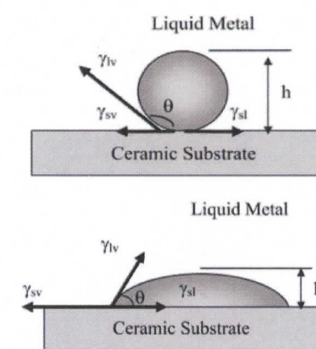
Technical Challenges in Bonding of Ceramics

- **Wetting of the Ceramic Substrate**
 - **Active Braze Alloys - Ti**

Contact Angle Between Ceramic and Liquid Filler Metal or Alloy

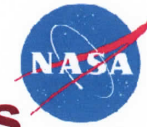
Ceramic Substrate	Filler Metal or Alloy	Temperature (°C)	Contact Angle (°)
SiC	Ag-28%Cu	930	160
SiC	Ag-35%Cu-1.5%Ti	850	10

Nascimento et al. Cerâmica 49 (2003) 178-198



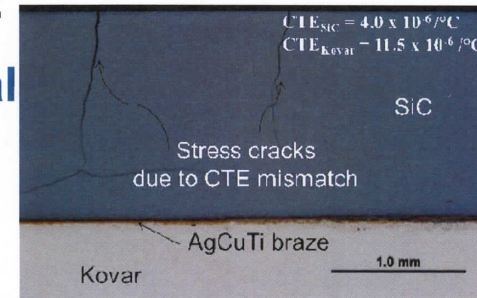
$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$

- **Residual stress due to differing CTE of substrate and braze**
 - **Delamination and cracking in SiC substrate**
 - **Control CTE of braze by dispersing SiC particulate**



Technical Challenges in Bonding of Ceramics to Metals

- Residual stress due to differing CTE
 - Major problem in joining SiC to metal



- Less severe in SiC-to-SiC joints but still important due to CTE mismatch between SiC and braze
- Control CTE of braze by dispersing SiC particulate



Background Information

➤ **C/C brazed to Ti-6Al-4V using SiC particles (4.6 μ m) in Ag-26.7Cu-4.6Ti**

Qin and Yu, Joining of C/C composite to TC4 using SiC particle-reinforced brazing alloy. Mater. Charact., 61, 2010, 635~639.

➤ **C/SiC brazed to metals using (Ag-6Al)+Ti+C filler (as mixture of Ag, Al, Ti powders and short carbon fibers)**

Wang et al, Reactive composite brazing of C_f/SiC composites to Ti alloy with (Ag-6Al)+Ti+C composite filler materials, Mater. Sci. Technol., 27(1), 2011, 49-52

➤ **C/SiC composite joined to Ti using Ag-Cu-Ti braze containing short carbon fibers**

Lin et al, Joints of carbon fiber-reinforced SiC composites to Ti-alloy brazed by Ag-Cu-Ti short carbon fibers, J. Mater. Proc. Technol., 189(1-3), 2007, 256-261

Main Findings:

- **Particles and fibers reacted with Ti, forming thin TiC_x layers**
- **Particles and fibers randomly distributed in braze**
- **Fibers preferentially aligned parallel to brazed interface**



Materials and Key Properties

Materials:

- Substrate: CVD silicon carbide
- Braze matrix: Ticusil (68.8Ag-6.7Cu-4.5Ti, T_L : 900°C)
- Braze reinforcement: SiC particulates (size: ~20 μm)

Generic Property Data

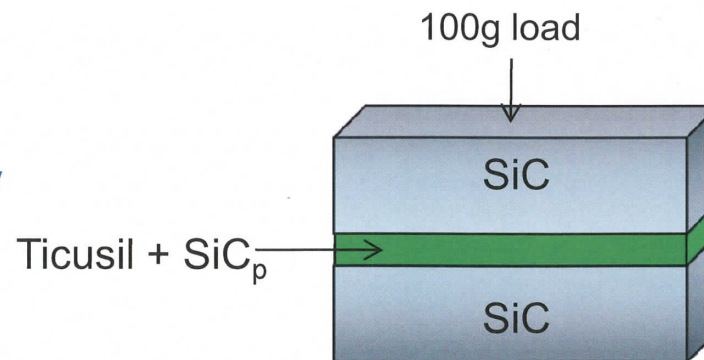
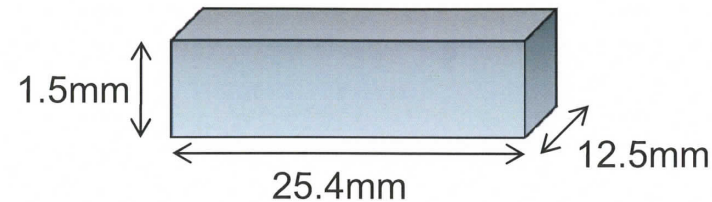
	E (GPa)	σ_y (MPa)	U.T.S. (MPa)	Thermal Conductivity (W/mK)	CTE ($\times 10^{-6}$ m/m*K)	Electrical Conductivity ($\times 10^6$ / Ωm)	% Elongation
Ticusil	85	292	339	219	18.5	29	28
SiC	466	-	-	300	4.0*	-	-

* 0 - 1000°C



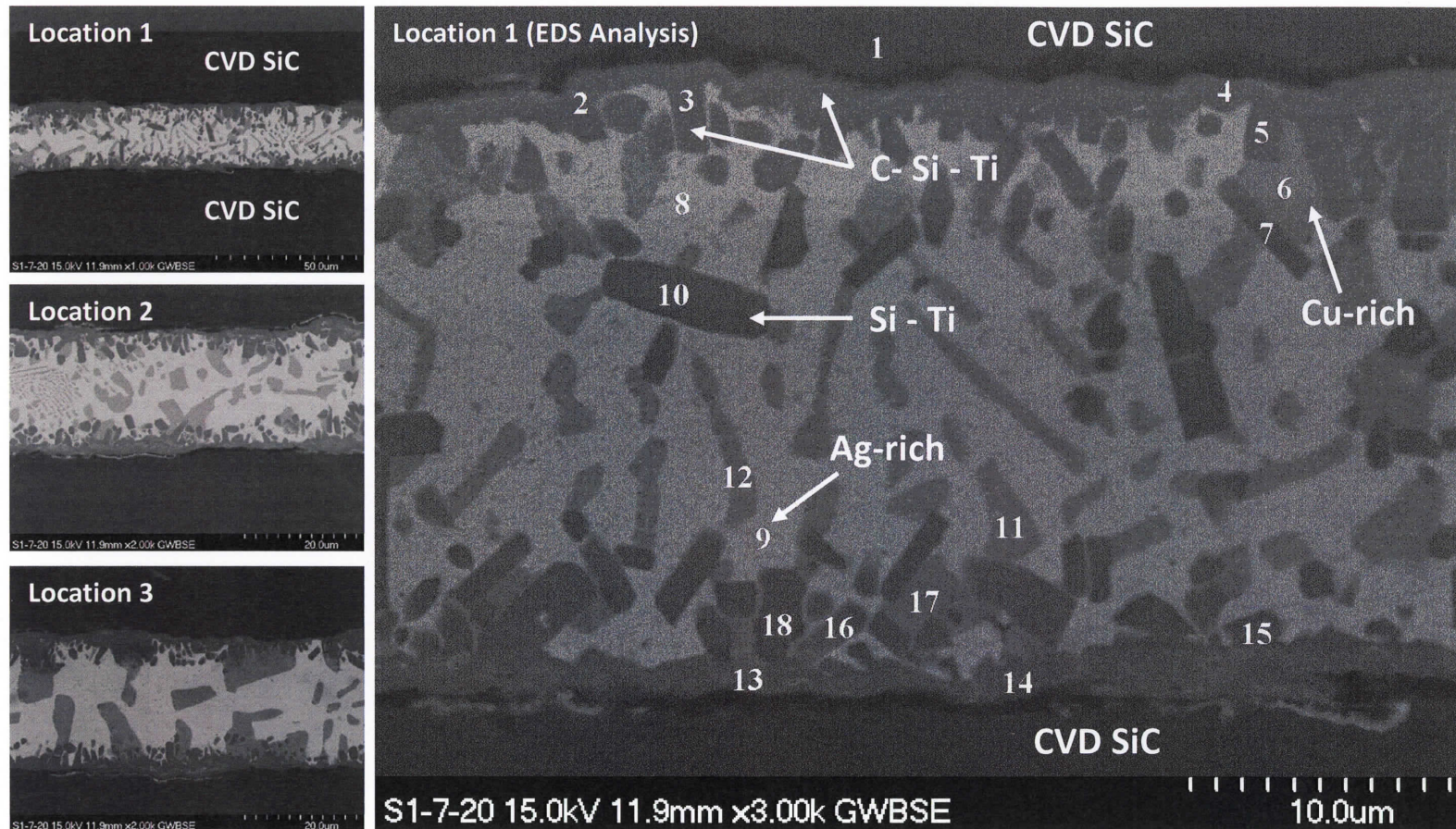
Experimental Procedures

- Ultrasonic cleaning of SiC substrate in Acetone for 10 min
- Ticusil powder mixed with 5, 10 and 15 wt% SiC particulates ($\sim 20 \mu\text{m}$) and glycerin to dough-like paste
- Paste applied using spatula and substrates sandwiched under 200g load
- Heated to 10°C above the braze liquidus temperature, isothermally held for 5 minutes
- Mounted in epoxy, polished and characterized



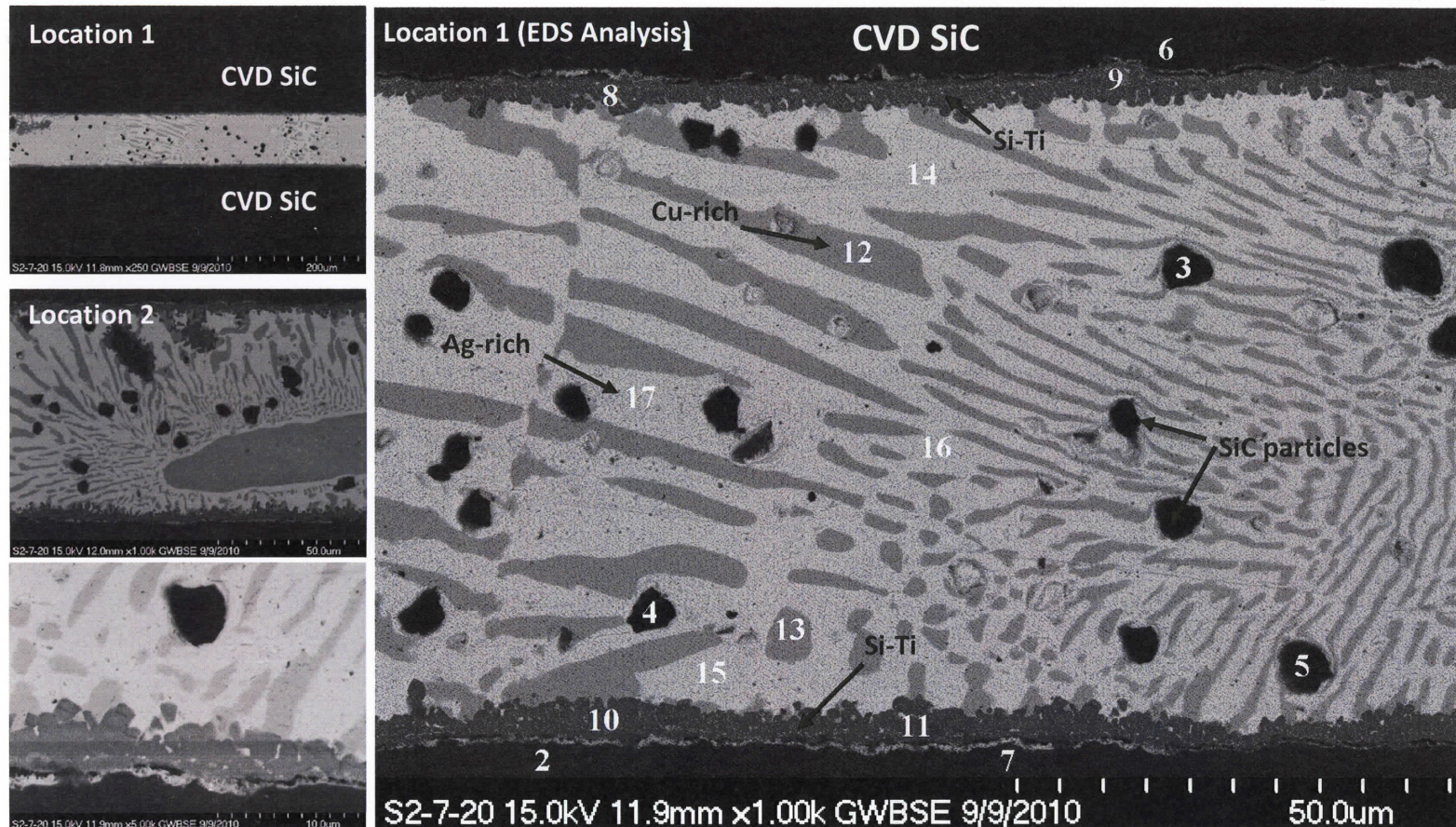


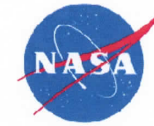
CVD SiC/Ticusil (0% SiCp)/CVD SiC



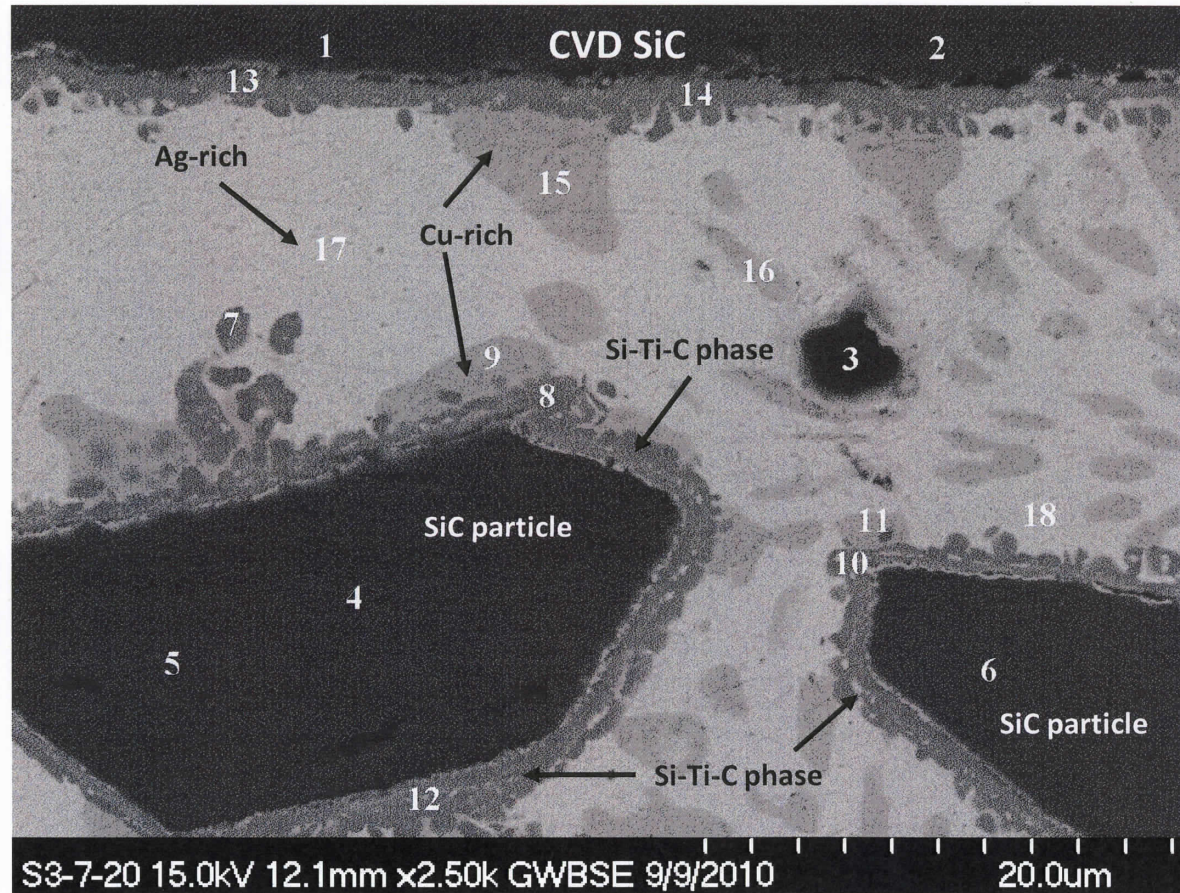
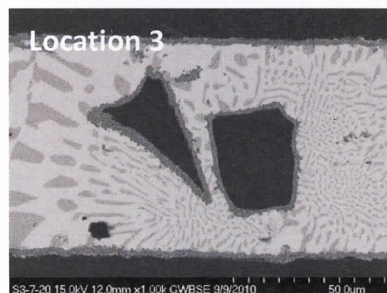
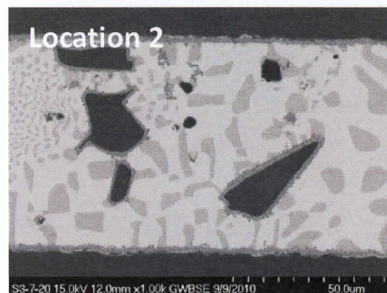
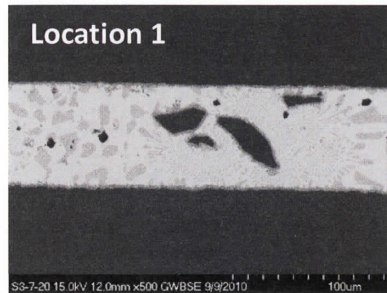


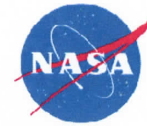
CVD SiC/Ticusil (5% SiCp)/CVD SiC



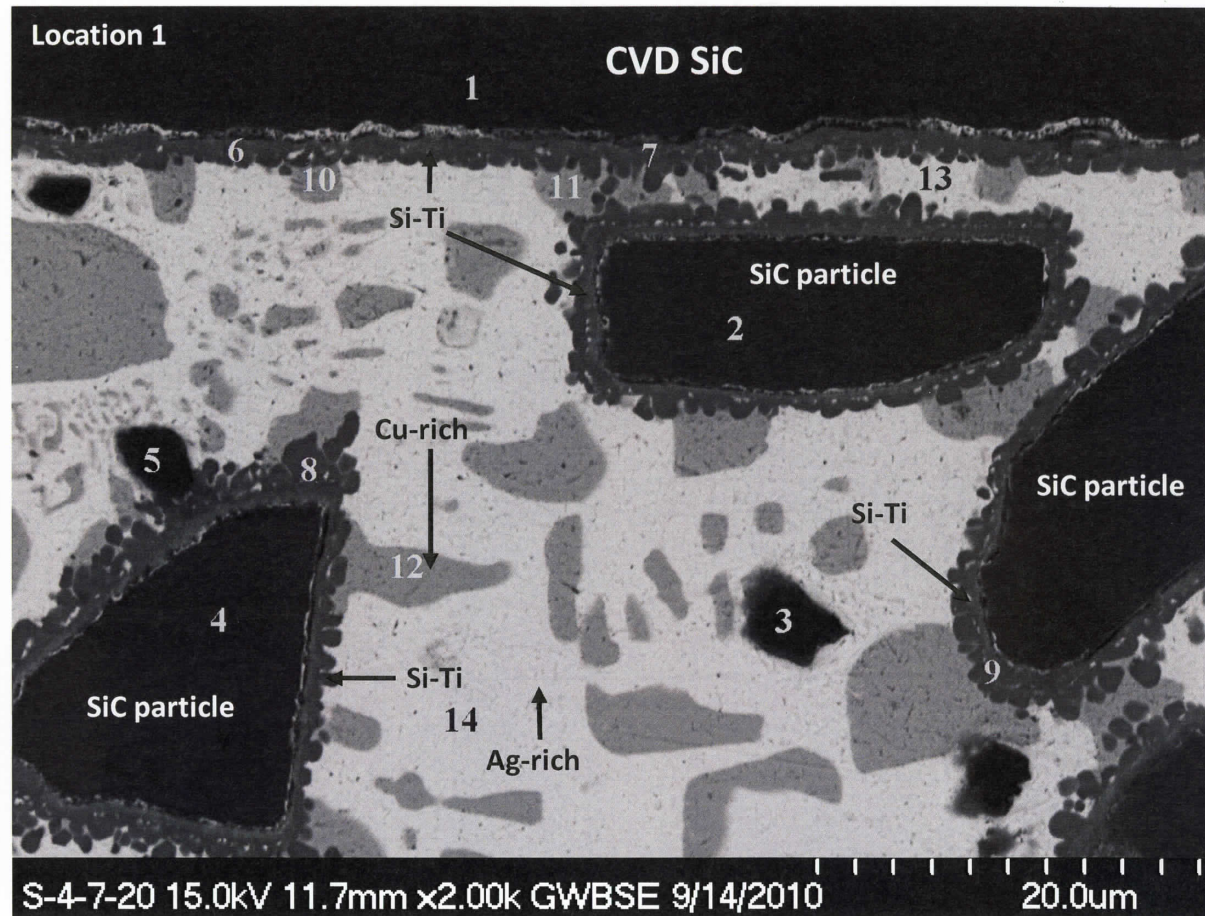
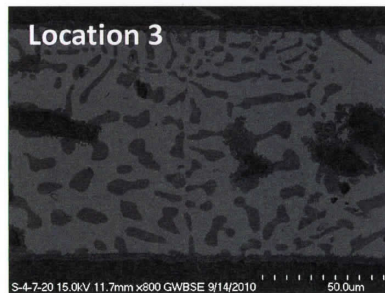
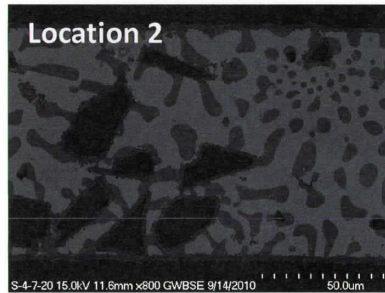
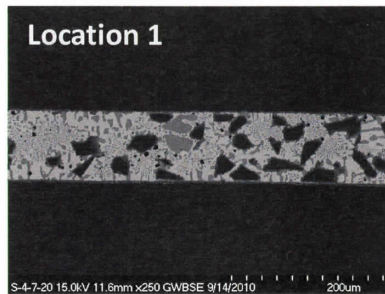


CVD SiC/Ticusil (10% SiCp)/CVD SiC





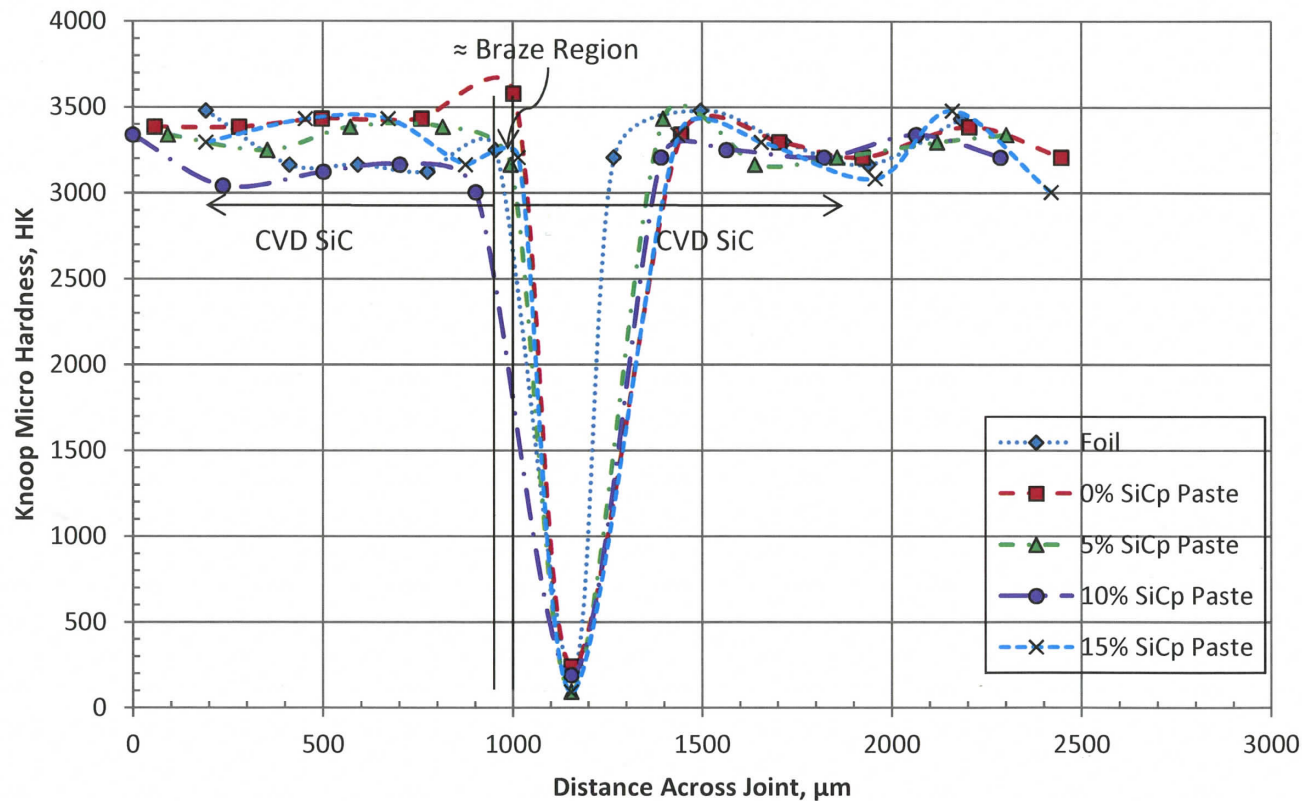
CVD SiC/Ticutil (15% SiCp)/CVD SiC





Effect of SiC Dispersion on Joint Hardness (Ticusil Braze)

SiC/Ticusil+SiC_p/SiC Joint



- *The small braze thickness allowed only a single indentation to be made within the braze.*
- *No measureable effect of SiC dispersion on joint hardness was noted*



Projected CTE Decrease with SiC Dispersion in Braze

Kerner's equation for volumetric CTE of a matrix containing particles:

$$\alpha_C = \alpha_m V_m + \alpha_p V_p - (\alpha_m - \alpha_p) V_m V_p \left[\frac{(1/K_m) - (1/K_p)}{(V_m/K_p) + (V_p/K_m) + (3/4G_m)} \right]$$

α_c = volumetric CTE of composite

α_m = volumetric CTE of matrix

α_p = volumetric CTE of particulate

V_m, V_p = volume fractions of matrix and particulate

K_m, K_p = Bulk moduli of matrix and particulate

G_m = Shear modulus of matrix

(E.H. Kerner, Proc. Phys. Soc., B69, 1956, 808)

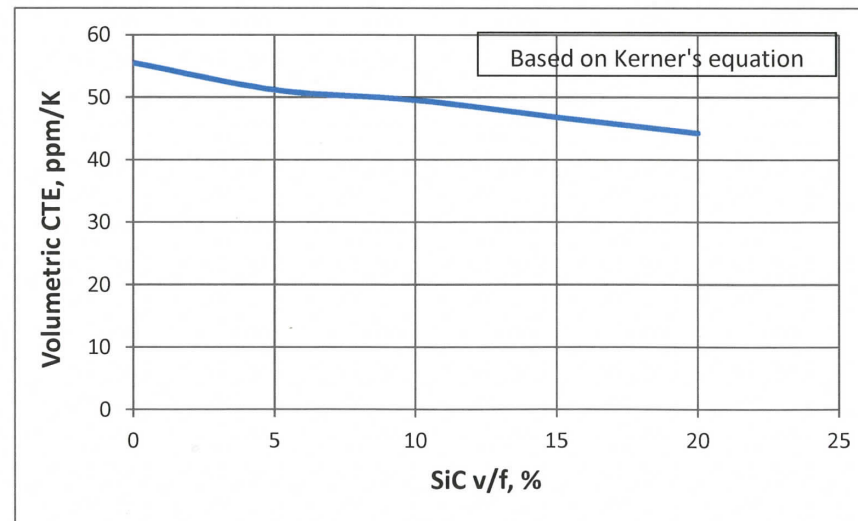
$$\alpha_m = 55.5 \times 10^{-6} \text{ K}^{-1}$$

$$\alpha_p = 12.3 \times 10^{-6} \text{ K}^{-1}$$

$$K_m = E/[3(1-2\nu)] = 57 \text{ GPa}, E = 85 \text{ GPa}, \nu \sim 0.25$$

$$K_p = 203 \text{ GPa}$$

$$G_m \sim 0.4E = 34 \text{ GPa}$$

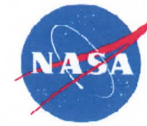


At 15 v/f SiC in Ticusil braze, a 16% decrease is projected in the CTE of Ticusil



Reaction and Interface Formation

- Formation of TiC and titanium silicides (TiSi_2 , Ti_5Si_3 , $\text{Ti}_5\text{Si}_3\text{C}_x$) is thermodynamically feasible ($\Delta G < 0$)
- Based on ΔG calculations, TiSi_2 and Ti_5Si_3 are less probable than TiC
- Titanium silicides could also form during solidification following SiC dissolution in braze and melt saturation with Si



Microstructural Observations

- SiC particles are randomly distributed in Ticusil and well-bonded
- Evidence of reaction of Ti with SiC and Ti-Si-C phase formation at interface
- SiC particles with Ti-rich interface aid nucleation of Cu-rich secondary phases
- Loss of Ti in reaction with SiC particulates did not impair bonding with SiC substrate
- Reinforcing AgCuTi braze with SiC can
 - *reduce the CTE mismatch and residual stresses*
 - *aid bonding*
 - *enhance braze strength*

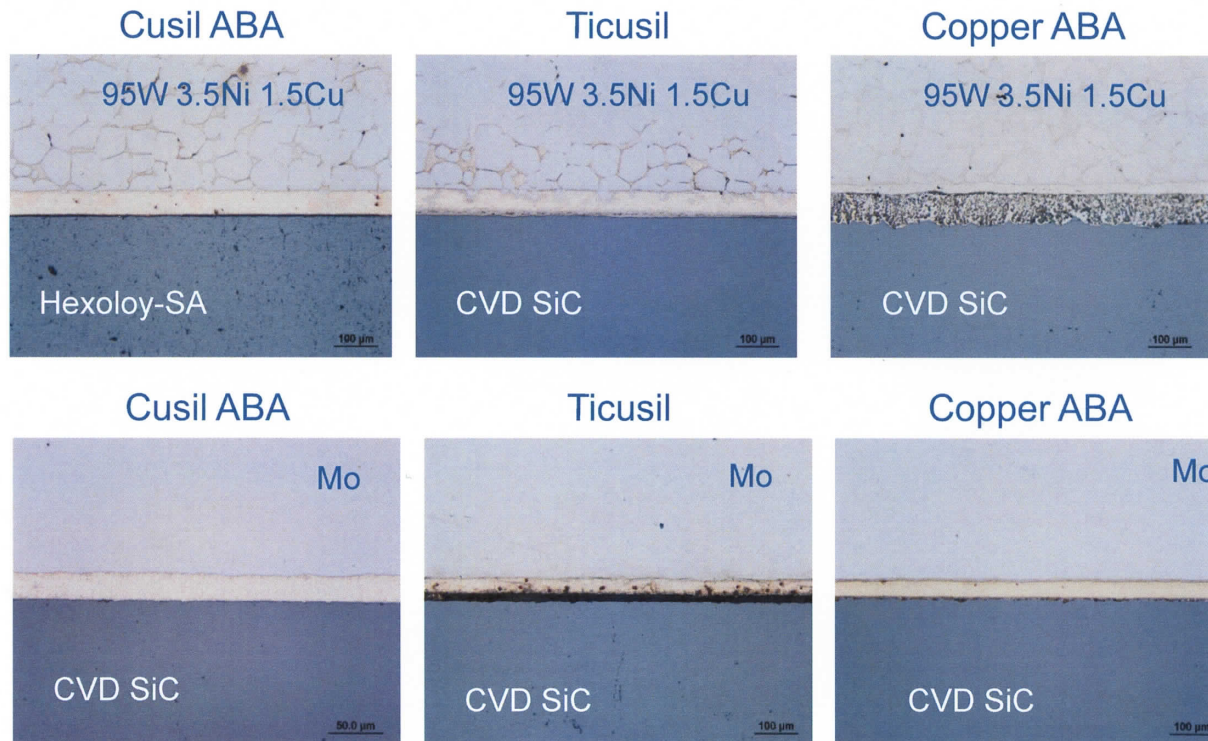


Observations

- **Loss in braze ductility from SiC dispersion and ability to accommodate stress may be compensated by CTE decrease**
- **Excessive addition of SiC particles may induce pores in the joint**
- **Fine SiC causes clustering, metal-starved cavities and sites for crack initiation**
- **At very high SiC content, more Ti in filler may be used up in reaction with SiC particulates, leading to thinner reaction layer at substrate interface and affecting the joint strength**

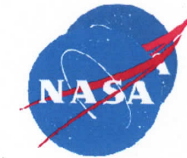


Bonding of Silicon Carbide-Metals (*ongoing...*)



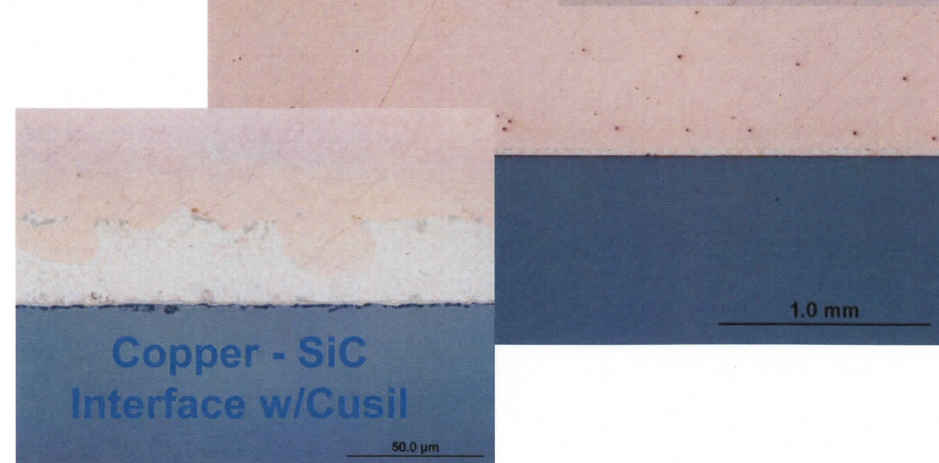
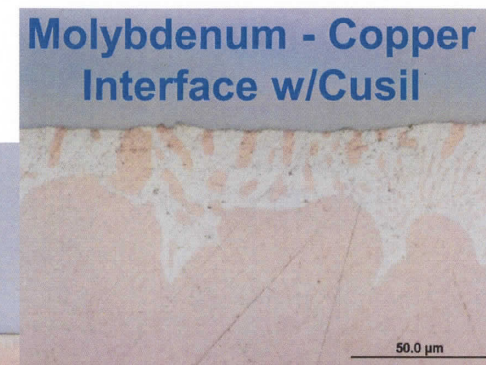
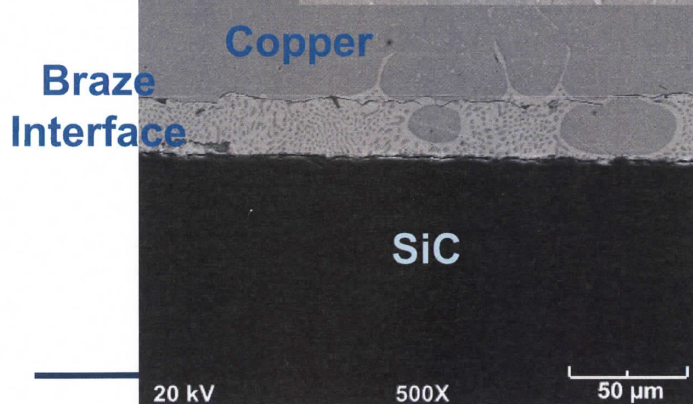
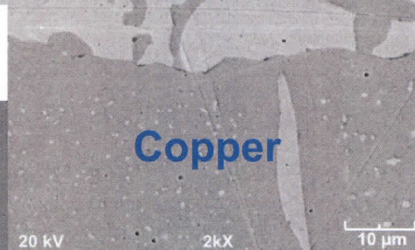
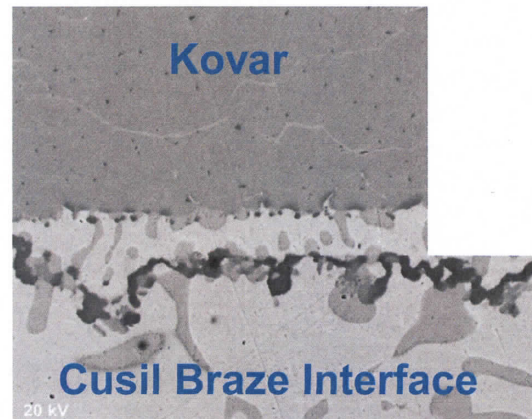
- SiC brazed to SiC, Ti, W, Ni, and Mo using Ag-Cu-Ti and Cu-Si-Al-Ti brazes
- Multilayer joints created to manage CTE induced residual stresses
- SiC-to-metal joints created using diffusion bonding were also extensively characterized for fuel injector application

Brazing of SiC to Kovar and to Molybdenum with Cusil ABA Foil/Copper/Cusil ABA Foil



Kovar / Cusil ABA / Copper /
Cusil ABA / SiC

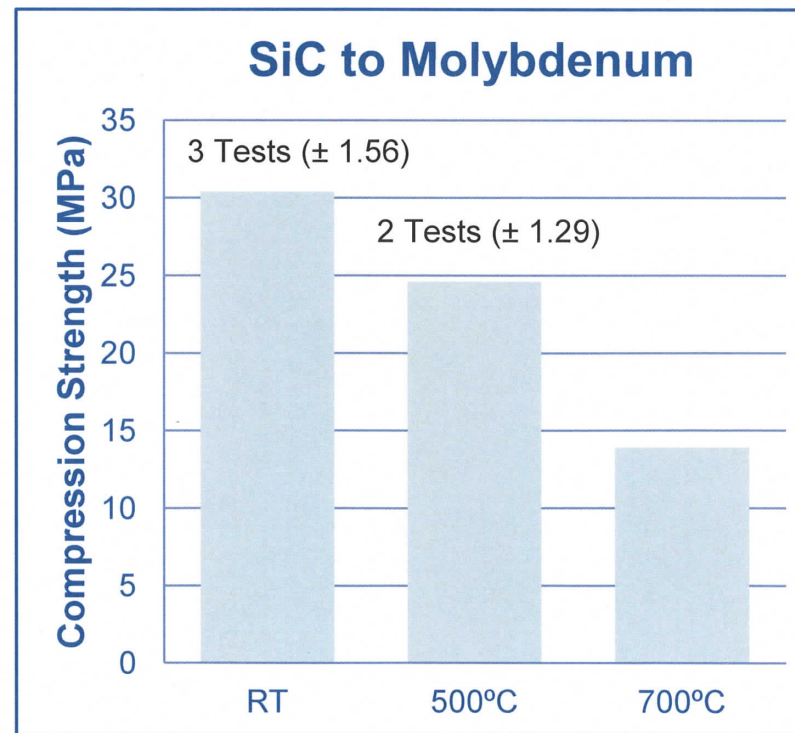
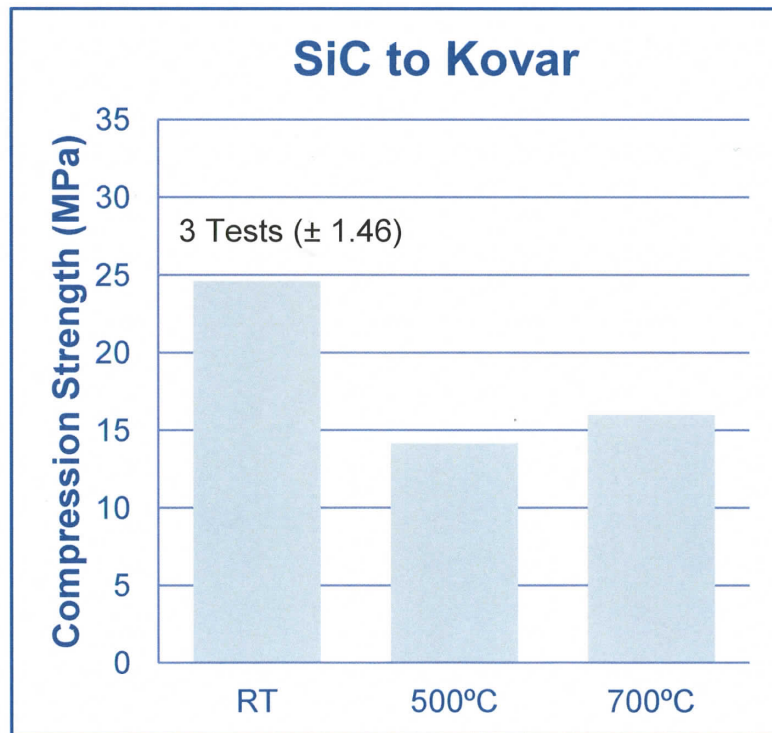
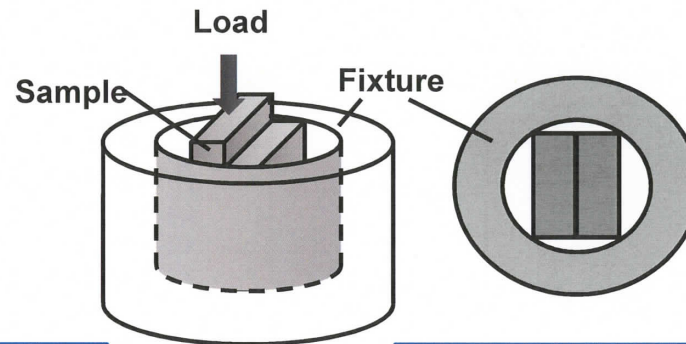
Molybdenum / Cusil ABA /
Copper / Cusil ABA / SiC





Shear Testing of SiC to Kovar and SiC to Molybdenum Joints with Copper and Cusil ABA Foil

- **Testing Conditions**
 - Crosshead speed: 0.5mm/min
 - Air
 - RT, 500°C, 700°C





Summary and Conclusions

- **Ti containing active brazes offer excellent wetting of the SiC substrates.**
- **SiC particulate reinforcements in Ticusil braze alloys can be used to reduced the thermal expansion and enhance braze strength.**
- **Copper interlayers proved to be capable of absorbing residual stresses introduced from brazing and acted as a diffusion barrier preventing unwanted silicide and carbide formation.**
- **Initial mechanical testing shows that Mo-SiC joints brazed with a copper interlayer are capable of high strength – failure typically occurred within the ceramic.**



Acknowledgements

- **This work was supported by the Subsonic Fixed Wing Project of the NASA Fundamental Aeronautics Program**
- **Bryan Coddington would like to thank LERCIP Program at NASA Glenn Research Center for summer research support**
- **Rajiv Asthana would like to thank OAI and NASA Glenn for summer research support**